Influence of Bound Polymer on Cure Characteristics of Natural Rubber Compounds Reinforced with Different Types of Carbon Blacks

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ABSTRACT: Rubber compounds are reinforced with fillers such as carbon black and silica. The cure characteristics of a filled rubber compound vary with the filler type and content. The influence of the type of carbon black on the cure characteristics of carbon black filled natural rubber compounds is investigated using two types of carbon black (N220 and N550), which are different in primary size and structure. The cure time and cure rate become faster as the carbon black content increases. The crosslink density also increases and reversion resistance is improved with the increase of carbon black content. The cure time and cure rate of the compound filled with N550 are faster than those of the compound filled with N220 at the same level of bound rubber content. In addition, higher crosslink density is also observed in the compound filled with N550 compared to that of the compound filled with N220 at the same level of bound rubber content. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2282–2289, 2005

Key words: cure characteristics; carbon black; bound rubber; filled rubber compound

INTRODUCTION

The types and contents of cure accelerators, the sulfur content, and the chemical properties of rubber affect the cure characteristics, such as the scorch time, cure rate, optimum cure time, and crosslink density.[1–8] The other factors affecting the cure characteristics are the type and content of fillers.[9–12] The cure rate of a filled rubber compound is faster than that of an unfilled one.[10,11] Silica-filled rubber compounds show slower cure characteristics compared to carbon black filled ones because silica adsorbs curatives.[13–16] In particular, the structure and surface chemistry of carbon black are known to affect the crosslink density and reversion resistance of the rubber compound.[9,10,17]

Bound rubber is an important factor in reinforcement; therefore, its phenomena and effects on the properties of filled rubber compounds and vulcanizates have been extensively studied.[18–22] The properties of bound rubber mainly depend on the characteristics of the filler such as the surface area, structure or morphology, and surface activity. In addition, the filler–polymer interactions leading to the formation of bound rubber are the physical adsorption, chemisorption, and mechanical interaction. Bound rubber is a parameter that is simple to measure, but the factors that influence the test results are very complicated.

The present work studied the influence of the content and type of carbon black on the cure characteristics of filled rubber compounds. The formation of bound rubber and its influence on the cure characteristics was especially focused using two types of carbon black as filler (N220 and N550). They were used as carbon blacks that are different in primary particle size and surface area. The properties of natural rubber (NR) compounds reinforced with N220 and N550 were compared.

EXPERIMENTAL

The carbon black filled NR compounds consisted of NR (SMR CV60), carbon black (N220 or N550), cure activators (stearic acid and ZnO), antidegradants [*N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine and wax], and curatives (*N*-*tert*-butyl-2-benzothiazole sulfenamide and sulfur). The filler contents were 20.0, 40.0, 60.0, 80.0, and 100.0 phr. N220 and N550, which have different primary particles and different structures, were employed as carbon blacks. The average diameters of the primary particles of N220 and N550 are about 20 and 50 nm, respectively. The dibutylphthalate (DBP) absorption value is used as the degree of filler structure, and the values are

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TABLE I
Formulations (phr)

	Compound number									
	1	2	3	4	5	6	7	8	9	10
SMR CV60[a]	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N220	20.0	40.0	60.0	80.0	100.0	0.0	0.0	0.0	0.0	0.0
N550	0.0	0.0	0.0	0.0	0.0	20.0	40.0	60.0	80.0	100.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HPPD[b]	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS[c]	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

[a] Standard Malaysian rubber.
[b] *N*-phenyl-*N′*-(1,3-dimethylbutyl)-*p*-phenylenediamine.
[c] *N*-*tert*-butyl-2-benzothiazole sulfenamide.

116.1 and 120.9 mL/100 g for N220 and N550, respectively. The formulations are given in Table I. The surface areas (nitrogen adsorption value) are 98.9 and 35.8 m^3/g for N220 and N550, respectively.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110°C for MB and 80°C for FM stages. The MB compounds were prepared by loading the rubber into the mixer and preheating for 0.5 min. The carbon black and ingredients were compounded into the rubber for 3.0 min and the resulting compounds were discharged. The FM compounds were prepared by mixing the MB compounds with the curatives for 1.5 min.

The Mooney viscosity at 100°C was measured with a Mooney MV 2000 viscometer from Alpha Technologies. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ±1.5 arc at 160°C. The contents of bound rubber were determined by extracting the unbound materials such as ingredients and free rubbers with toluene for 7 days and *n*-hexane for 1 day followed by drying for 2 days at room temperature. The weights of the samples before and after the extraction were measured and the bound rubber contents were calculated according to eq. (1):

$$R_b(\%) = 100 \times [W_{fg} - W_t[m_f/(m_f + m_r)]]/W_t[m_r/(m_f + m_r)] \quad (1)$$

where R_b is the bound rubber content, W_{fg} is the weight of filler and gel, W_t is the weight of the sample, m_f is the fraction of the filler in the compound, and m_r is the fraction of the rubber in the compound.

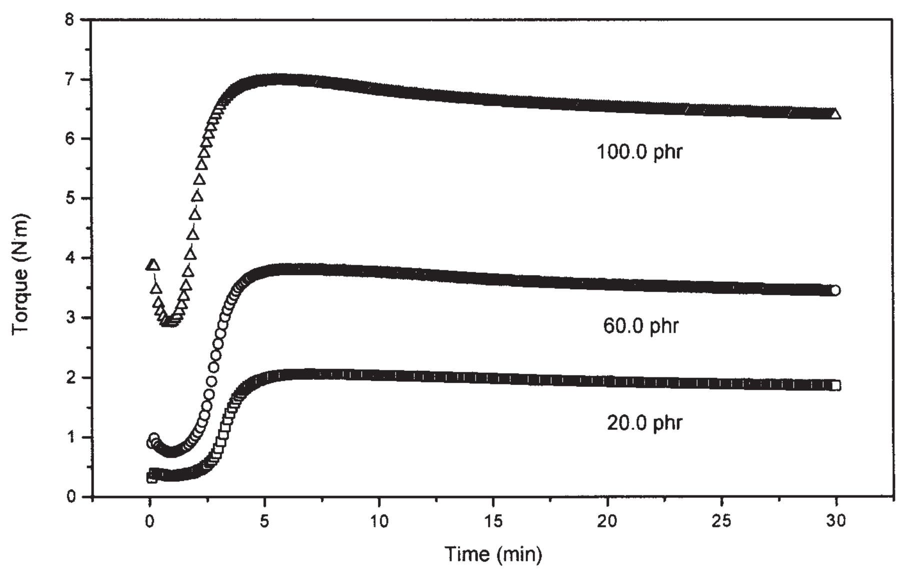

Figure 1 Rheographs at 160°C of the compounds filled with N220 contents of (□) 20.0, (○) 60.0, and (△) 100.0 phr.

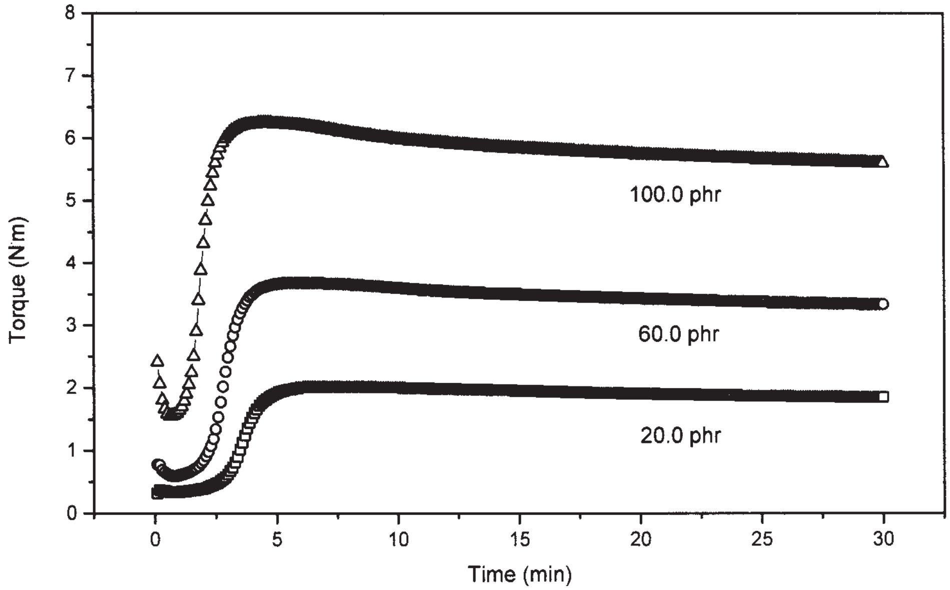

Figure 2 Rheographs at 160°C of the compounds filled with N550 contents of (□) 20.0, (○) 60.0, and (△) 100.0 phr.

RESULTS AND DISCUSSION

Figures 1 and 2 show the rheographs at 160°C. The minimum torque (T_{min}) and maximum torque (T_{max}) increase with increases in the carbon black content. The Mooney viscosity of the compound increases steeply as the filler content increases (Fig. 3). The viscosity of the N220-filled compound is higher than that of the N550-filled one. In addition, the increased viscosity for the compounds filled with N220 is slightly more sensitive to the filler content. This arises from the difference in the bound rubber contents. The variation of the bound rubber content with the filler content is shown in Figure 4. The viscosity of the compound filled with 100.0 phr N220 could not be measured because the viscosity was too high. The Mooney viscometer has a viscosity limit of 200 Mooney units. The bound rubber content of the N220-filled compound is higher than that of the N550-filled one. This is due to the surface area of N220 being about 3 times higher than N550, as described in the Experimental section. The bound rubber contents in both of the compounds are almost proportional to the filler content. The bound rubber content increases by about 6.9 and 4.5% for every 10.0 phr increase of the filler content for N220 and N550, respectively. However, considering the difference in the surface areas between the two types of carbon black, the degree of increased bound rubber content for the N220-filled compound is not much higher than that of the N550-filled one.

The bound rubber content in a filled rubber compound is an indication of how to determine the level of reinforcement. The variation of the viscosity replotted as a function of the bound rubber content shows the direct influence of the bound rubber content on the viscosity (Fig. 5). The compounds reinforced with N550 are more sensitive to the viscosity than the compounds filled with N220 in terms of the bound rubber

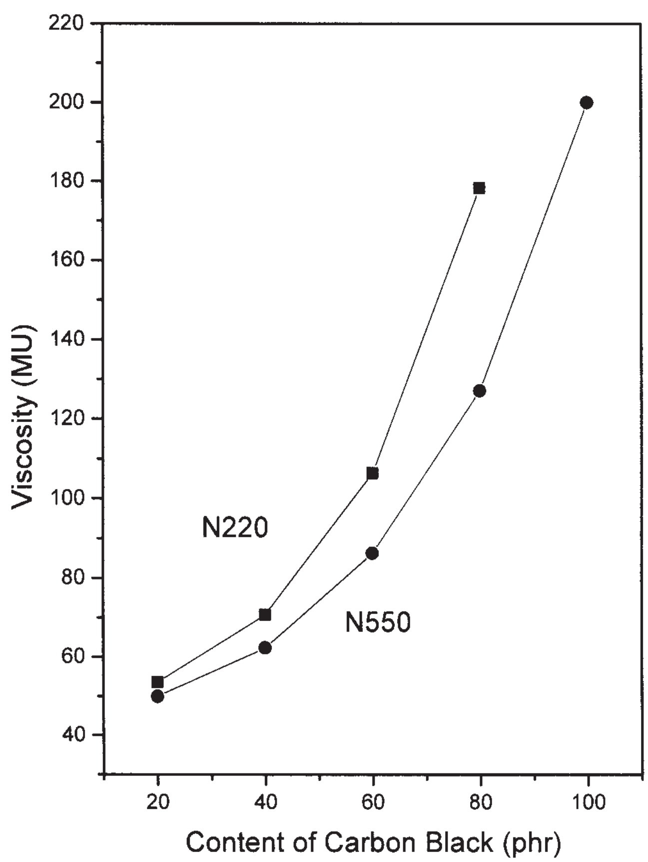

Figure 3 The variation of the Mooney viscosity (ML 1 + 4 at 100°C) as a function of the content of carbon black in the compounds filled with (□) N220 and (○) N550.

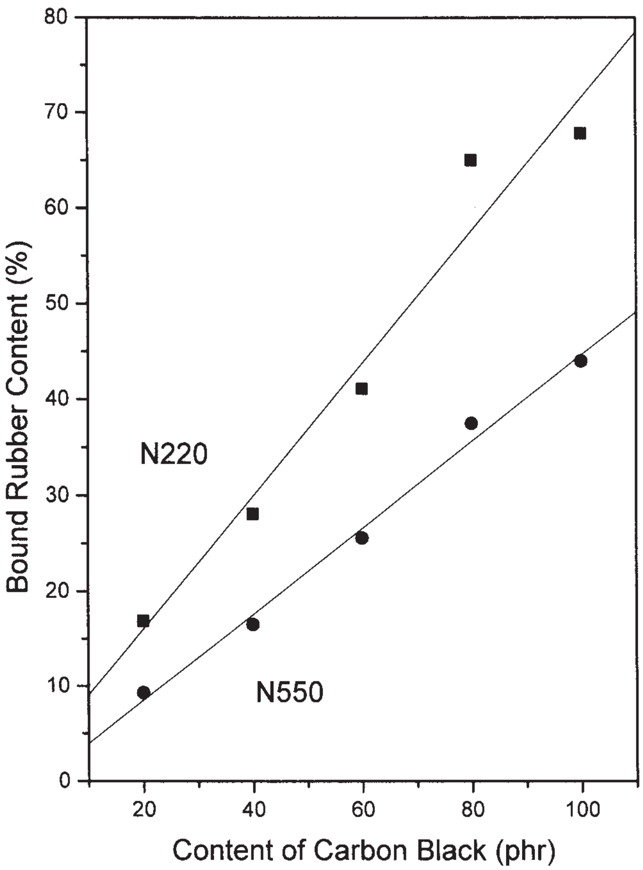

Figure 4 The variation of the bound rubber content with the content of carbon black in the compounds filled with (□) N220 and (○) N550.

content. This is an opposite trend to Figure 3, which is the variation of the viscosity with the filler content. This reverse trend is explained by the fact that N550 has a more developed structure than N220, whereas the surface area of N550 is much smaller than that of N220. A higher DBP value means a more developed filler structure, so the DBP values also support this explanation. The DBP values of N220 and N550 are 116.1 and 120.9 mL/100 g, respectively. Bound rubbers consist of tightly and loosely bound rubbers.[23–25] In general, a carbon black with a more developed structure has more tightly bound rubber than a carbon black with a less developed one. The loosely bound rubber exists in an outer shell around the filler whereas the tightly bound rubber is in the immediate vicinity of the filler particle. The tightly bound rubber is much less mobile than the loosely bound rubber. The contents of tightly bound rubber were measured at 90°C. Portions of the tightly bound rubber of the total bound rubber content are 46–49 and 50–57% for the compounds reinforced with N220 and N550, respectively (filler content = 60–100 phr). These differences in the portion of tightly bound rubber also explain the higher viscosity of the N550-filled compound in the plot as a function of the bound rubber content (Fig. 5).

The cure times become faster as the filler content increases (Fig. 6). The t_2, t_{40}, and t_{90} cure times in the rheograph are the times taken for the torque to reach from the T_{min} to increases of 2, 40, and 90% of the change in the torque ($\Delta T = T_{max} - T_{min}$), respectively. The curve-fitting equations in Figure 6 show good linear correlations. Results from the curve-fitting process are summarized in Table II. The cure times of the compounds filled with N550 are more sensitive to the filler content than those of the compounds filled with N220. The t_{40} and t_{90} values for the compounds filled with N550 at about 0.19 and 0.23 min, respectively, become faster for every 10.0 phr increase of the filler content whereas for the compounds filled with N220 they are about 0.16 and 0.17 min, respectively.

Variations of the cure times were also replotted as a function of the bound rubber content to investigate the influence of the bound rubber content in detail. Figure 7 shows a big difference in the sensitivity of the cure times to the bound rubber content between the compounds filled with N220 and N550. The cure times of the compounds filled with N550 are about twice as sensitive to the bound rubber content than those of the

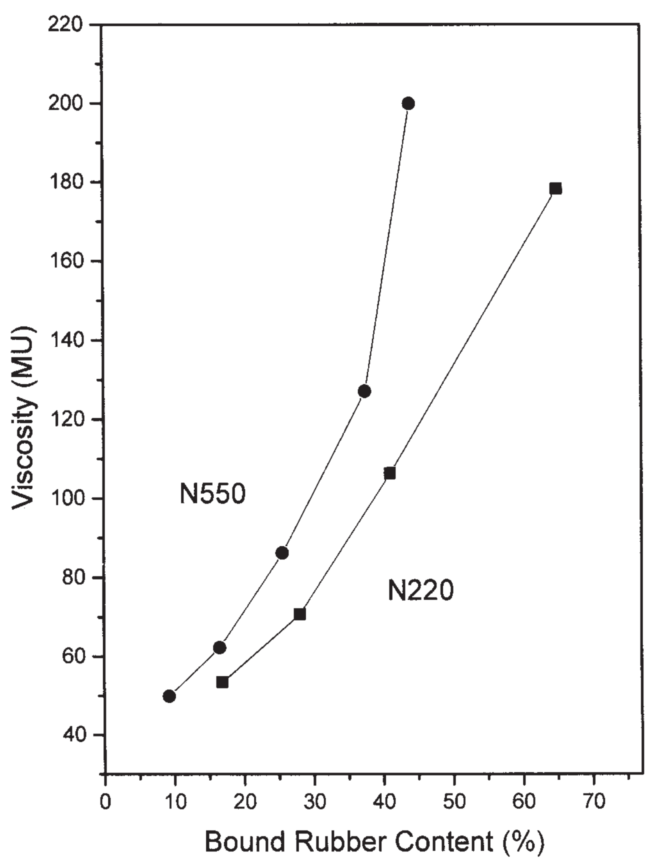

Figure 5 The variation of the Mooney viscosity (ML 1 + 4 at 100°C) as a function of the bound rubber content in the compounds filled with (□) N220 and (○) N550.

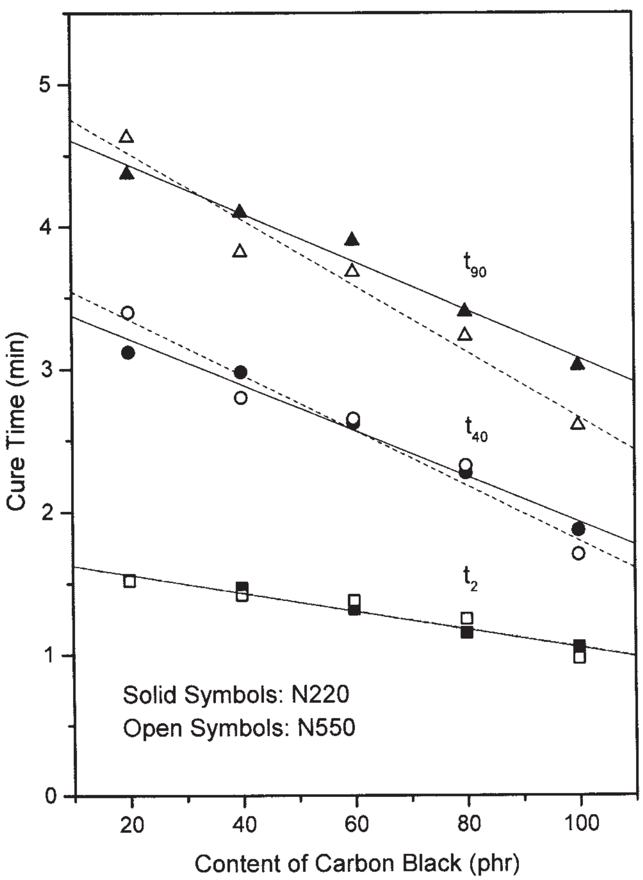

Figure 6 The variation of the cure times as a function of the content of carbon black in the compounds filled with (▲, ●, ■) N220 and (△, ○, □) N550 the (■, □) t_2 (●, ○) t_{40}, and (▲, △) t_{90}. respectively.

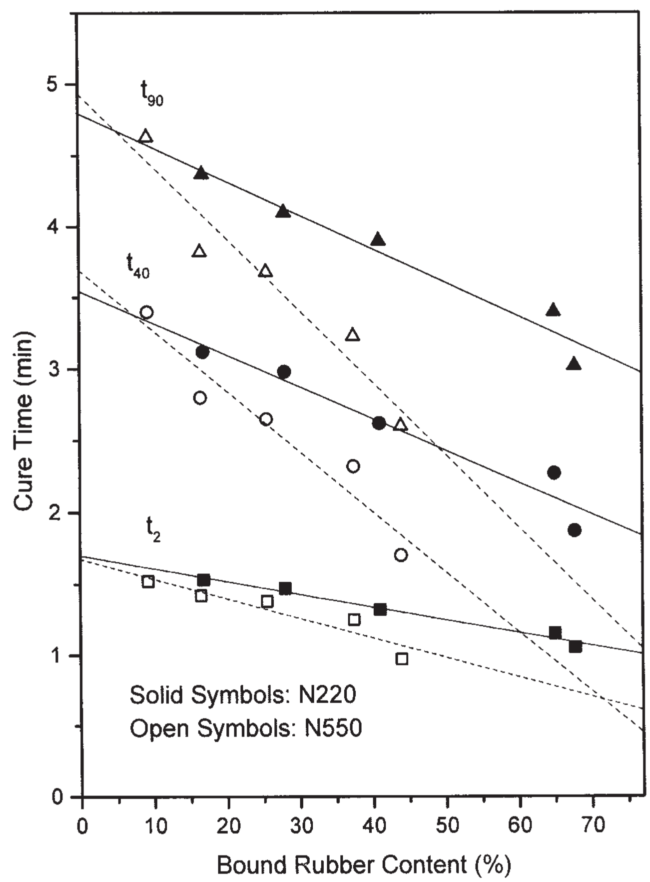

Figure 7 The variation of the cure times as a function of the bound rubber content for the compounds filled with (▲, ●, ■) N220 and (△, ○, □) N550 at (■, □) t_2, (●, ○) t_{40}, and (▲, △) t_{90}.

compounds filled with N220. The t_2, t_{40}, and t_{90} values for the compounds filled with N550 at about 0.14, 0.42, and 0.50 min, respectively, become faster for every 10.0% increase of the bound rubber content whereas the values for the compounds filled with N220 are about 0.09, 0.22, and 0.24 min, respectively. This can also be explained by the more developed structure of N550 compared to N550. Thus, the compound reinforced with N550 has more the tightly bound rubber than the compound reinforced with N220. The tightly bound rubber in the immediate vicinity of the carbon black is likely to impede the curative adsorption on

TABLE II
Curve-Fitting Equations for Cure Characteristics (N220/N550)

Cure characteristics	Variable	Slope[a]	Correlation coefficient[b]
t_2	Carbon black content	−0.0064/−0.0064	−0.99/−0.95
	Bound rubber content	−0.0090/−0.0138	−0.99/−0.93
t_{40}	Carbon black content	−0.0161/−0.0194	−0.99/−0.98
	Bound rubber content	−0.0222/−0.0421	−0.97/−0.96
t_{90}	Carbon black content	−0.0170/−0.0233	−0.99/−0.98
	Bound rubber content	−0.0237/−0.0505	−0.98/−0.97
Cure rate	Carbon black content	0.0164/0.0251	0.99/0.98
	Bound rubber content	0.0228/0.0550	0.98/0.98
Change in torque	Carbon black content	0.0308/0.0382	0.99/0.99
	Bound rubber content	0.0435/0.0842	0.99/0.99

[a] The slope data were obtained from the curve-fitting equations.
[b] The first and second values are for the compounds reinforced with N220 and N550, respectively.

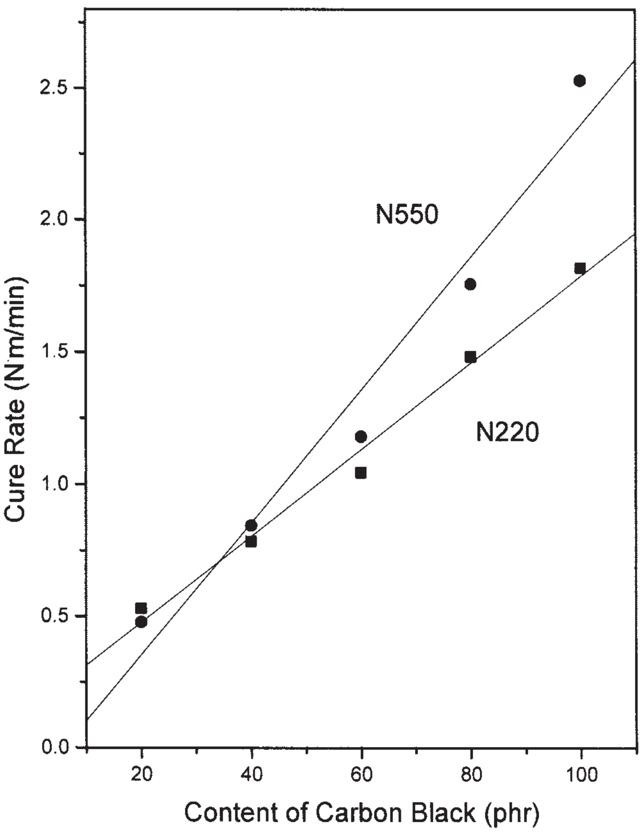

Figure 8 The variation of the cure rate as a function of the content of carbon black at a cure rate of $(T_{90}-T_2)/(t_{90}-t_2)$ for compounds filled with (■) N220 and (●) N550.

the filler surface. The effective prevention of curative adsorption allows more free curatives to be available in rubber matrix, and then the crosslinking reactions become faster.

The cure rate is also increased by increasing the filler content (Fig. 8). It was calculated by dividing the difference between the torques at t_{90} and t_2 (T_{90} and T_2, respectively) by the difference at t_{90} and t_2, that is, cure rate = $(T_{90} - T_2)/(t_{90} - t_2)$. The cure rate also increases linearly with the increase in the filler content, as shown in Figure 8 and Table II. The cure rate of the compound filled with N550 is also more sensitive to the filler content than the compound filled with N220. The cure rates of the compounds filled with N220 and N550 increase about 0.16 and 0.25 Nm/min, respectively, for every 10.0 phr increase of the filler content. Figure 9 shows the variation of the cure rate as a function of the bound rubber content. The difference in the sensitivity of the cure rate to the bound rubber content is larger than in the sensitivity to the filler content. The cure rates of the compounds filled with N220 and N550 increase about 0.23 and 0.55 Nm/min, respectively, for every 10.0% increase of the bound rubber content. This can be explained by the tightly bound rubber as discussed previously. A rubber compound with more free curatives available shows a faster cure rate than with lower free curatives available.

Figure 10 shows the variation of the T_{min}, T_{max}, and ΔT with the filler content. The torques increase with increases in the filler content. Variations of the T_{min} and T_{max} do not show linear correlations. The T_{min} and T_{max} increase sharply at high filler content regions. This is due to the high viscosity of the highly filled compound. The steeply increased viscosity was discussed previously (Figs. 3, 5). In contrast, the variation of the ΔT shows a good linear correlation (Table II). Correlation coefficients for the curve-fitting equations of the ΔT are about 0.99. The torque of the compounds filled with N220 and N550 increase about 0.31 and 0.38 N m, respectively, for every 10.0 phr increase of the filler content. The ΔT of the compound filled with N550 is more sensitive to the filler content than for the compound filled with N220. The difference is more clear in the variation of the ΔT with the bound rubber content (Fig. 11). The ΔT values of the compounds filled with N220 and N550 increase about 0.43 and 0.84 N m, respectively, for a 10% increase in the bound

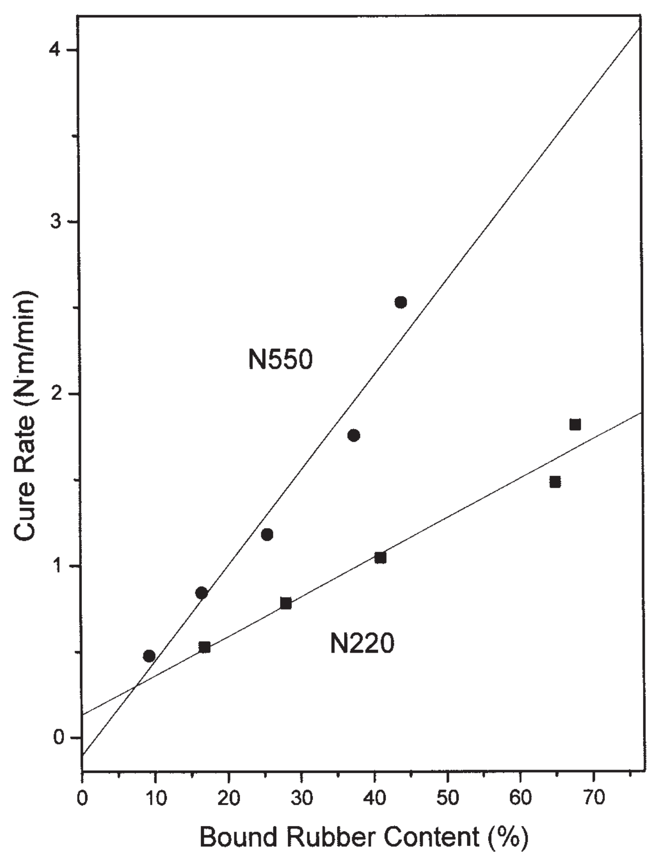

Figure 9 The variation of the cure rate as a function of the bound rubber content at a cure rate of $(T_{90}-T_2)/(t_{90}-t_2)$ for compounds filled with (■) N220 and (●) N550.

rubber content. This can also be explained by the tightly bound rubber as discussed previously. A rubber compound with higher content of curatives shows a higher crosslink density than that with a lower one. The change in the torque of a rubber compound directly reflects the crosslink density, which in turn depends on the amount of free curatives available in the compounds.

CONCLUSIONS

The viscosity increased with increases in the filler content. The cure time and cure rate became faster as the filler content increased. The torques in the rheograph also increased with increases in the filler content. These were explained by the increased bound rubber content. The variations of the cure characteristics of the compounds filled with N550 were more sensitive to the filler content and the bound rubber content than the compounds filled with N220. The difference in the sensitivity of the cure characteristics to the filler and bound rubber contents for the compounds reinforced with N220 and N550 were explained by the structure of carbon black and the tightly bound rubber that reduced the curative adsorption on carbon black.

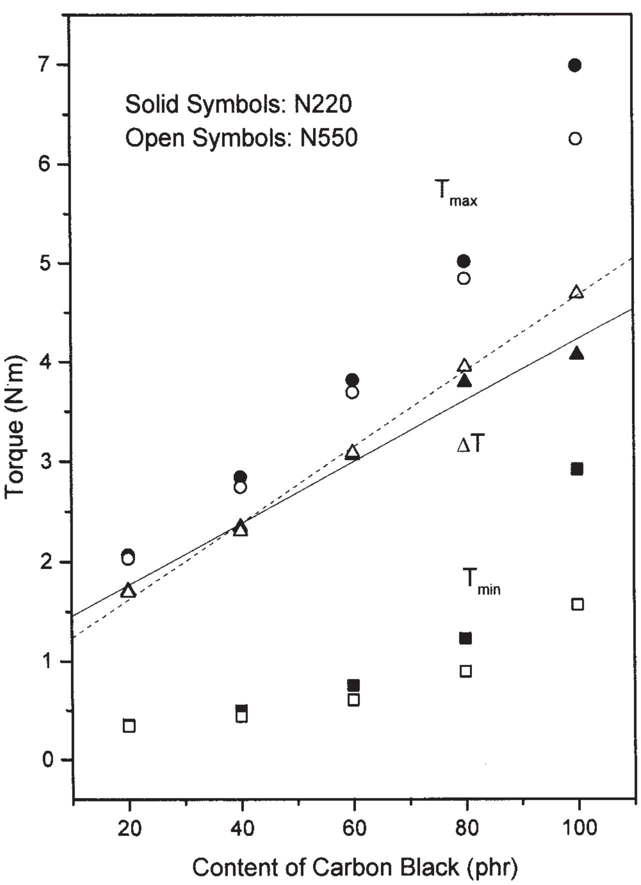

Figure 10 The variation of the torque as a function of the content of carbon black for compounds filled with (●, ▲, ■) N220 and (○, △, □) N550 at (■, □) minimum torque (T_{min}), (●, ○) maximum torque (T_{max}), and (▲, △) change in torque ($\Delta T = T_{max} - T_{min}$).

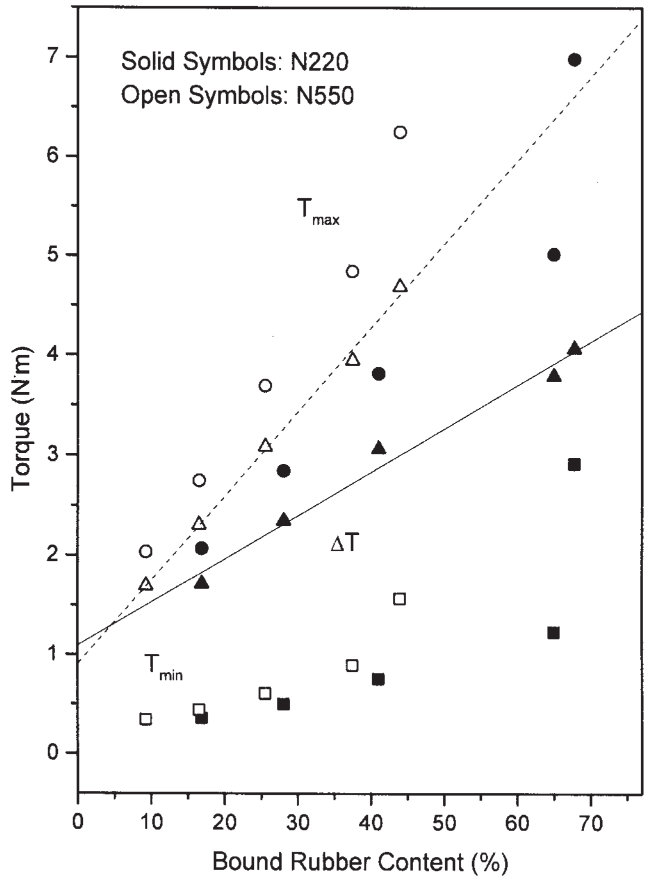

Figure 11 The variation of the torque as a function of the bound rubber content for compounds filled with (●, ▲, ■) N220 and (○, △, □) N550 at (■, □) minimum torque (T_{min}), (●, ○) maximum torque (T_{max}), and (■, □) change in torque ($\Delta T = T_{max} - T_{min}$).

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